VIBRATIONAL DYNAMICS OF TRIFLUOROACETIC ACID AND FORMIC ACID IN GAS AND DILUTE SOLUTION: CRACKING OPEN GAS PHASE ACID DIMERS

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Ultrafast time-domain transient absorption spectroscopy is used to study the vibrational dynamics of the cyclic hydrogen bonded dimers of trifluoroacetic acid and formic acid in both the gas- and solution-phase. Deposition of energy into the broad dimer bands of these acid dimers in the gas-phase provides the means to break open the dimer, as evidenced by the growth of a ``free O-H´´ absorbance at ~3580$\mathrm{cm}^{-1}$on the time scales of energy flow out of the initially excited dimer region. In trifluoroacetic acid there is no change in the rate of ``free O-H´´ growth with varying pump frequency between 2596$\mathrm{cm}^{-1}$and 3131cm^{-1}. Spectrally resolved pump-probe experiments are performed to reveal the evolution of a broad range of the spectra in time, which facilitates interpretation of the dynamics behind the time scales provided by single frequency measurements. When the acid dimers are solvated (0.05M CCl_4 solution), energy pumped into the broad dimer band can be cooled out by the solvent, making it unavailable to the process of dimer opening.